



THE RELATIONSHIP BETWEEN
SULFATE AIR QUALITY AND
VISIBILITY AT LOS ANGELES

by

GLEN R. CASS

EQL MEMORANDUM NO. 18

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Environmental Quality Laboratory
CALIFORNIA INSTITUTE OF TECHNOLOGY
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NOTE

The statements and conclusions in this report are those of the Contractor and not necessarily those of the State Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

ABSTRACT

Routine air monitoring data taken by the Los Angeles Air Pollution Control District are related to visibility at downtown Los Angeles over the decade 1965 through 1974. The relationship between light extinction and total suspended particulate mass implied by the historical data base is shown to be consistent with the findings of previous short-term special studies.

A non-linear regression model for light extinction at Los Angeles is constructed which combines available information on aerosol chemical composition with relative humidity and NO_2 data. It is shown that there is a pronounced increase in light scattering per unit sulfate solute mass on days of high relative humidity, as would be expected for a hygroscopic or deliquescent substance.

Using the chemically resolved regression model, estimates are made of the long-run visibility impact of reducing sulfates to one half and to one quarter of their measured historic values on each past day of record. It is found that the effect of such a sulfate concentration reduction would have been manifested most clearly in a decline in the number of days per year with average visibility less than three miles. The number of days per year with average visibility less than ten miles would be little affected. One reason for the disproportionate impact of sulfates on the days of the worst visibility is found in the high positive correlation between sulfate mass concentration and relative humidity. High values of light scattering per unit sulfate mass thus occur on days of high sulfate mass concentration.

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Introduction

The problem at hand is to determine the relationship between atmospheric sulfate concentrations and visibility reduction at downtown Los Angeles over the past decade. Severe visibility deterioration is one of the most readily apparent features of the Los Angeles smog syndrome. During the 25-year period since 1950, prevailing visibilities of less than three miles at relative humidities below 70 percent have been observed at downtown Los Angeles on an average of 100 days per year (Birakos, 1974). Recently completed short-term studies of particulate air quality in relation to visibility (Hidy, et al., 1975; White and Roberts, 1975) indicate that sulfates in the Los Angeles atmosphere are much more effective light scatterers per unit mass than other particulate components, and that sulfates may be responsible for over half of the light scattering at downtown Los Angeles.

The findings of White and Roberts have important implications for a strategy aimed at improving visibility in Los Angeles. A particulate control strategy for the Los Angeles basin proposed by Trijonis, et al. (1975), involving reduction of sulfates and nitrates from annual average levels of 14 micrograms per cubic meter $\text{SO}_4^{=}$ and 12 micrograms per cubic meter NO_3^{-} to levels of 6.1 and 10 micrograms per cubic meter annual mean, respectively, was estimated to cost approximately 156 million dollars annually. If such pollution control measures were to be proposed in part on the basis of visibility improvement, it is important to determine if the relationship observed by White and Roberts (1975) is persistent, and not simply an anomaly of the few days on which their samples were taken.

A brief discussion of the causes of light extinction in the atmosphere will serve as the basis for structuring a statistical model for visibility at Los Angeles. The model will then be applied to the routine air monitoring data base of the Los Angeles Air

Pollution Control District over the historic period August 1965 through December 1974. Empirical results will be compared to theory and to the more detailed observations of others where possible. Then the model will be used to estimate the impact of reduced levels of particulate sulfates in the atmosphere on the cumulative distribution of daily visibilities at Los Angeles.

Visibility in Theory and by Observation

Attenuation of light intensity, I , by a column of air over distance, x , can be used to define an extinction coefficient, b , for that air parcel in accordance with the Beer-Lambert law:

$$(1) \quad \frac{dI}{I} = -b \, dx$$

In his classical visibility theory, Koschmieder (1924) proposed a relationship between this extinction coefficient b (which is a property measurable by instrumental methods) and the maximum distance at which an average individual could distinguish an ideal black object silhouetted against the horizon sky. By assuming that a contrast level of 0.02 was the lower limit distinguishable to the human eye, Koschmieder was able to define a theoretical maximum visual distance, now known as "meteorological range", L_v , by:

$$(2) \quad L_v = \frac{-\ln 0.02}{b} = \frac{3.912}{b} \quad \text{in consistent units.}$$

Visibility apparent to an individual observer can differ from Koschmieder's theoretical result due to a number of factors including variation in the observers' visual acuteness and the inhomogeneous illumination of the atmosphere. Thus it is useful to consider a more personal measure of visibility, called "visual range", which is defined as the actual distance at which an ideal black object can just be seen against the horizon sky. To partially account for spatial variation in the optical properties of the atmosphere, daylight visual

range observations made in accordance with National Weather Service standards are stated in terms of a "prevailing visibility". Prevailing visibility is defined as the greatest visibility which is attained or surpassed around at least half of the horizon circle, but not necessarily in continuous sectors (Williamson, 1973). A discussion of the possible errors involved in using Koschmieder's formula to estimate visibility apparent to a human observer is given by Horvath (1971). He suggests that by proper selection of visibility markers it should be possible to use the Koschmieder formula to calculate the extinction coefficient from observed visibilities with an error of less than about ten percent.

Relating Visibility to Atmospheric Composition

From expression (2), it is seen that the larger the extinction coefficient, b , the lower the expected visibility. This extinction coefficient is depicted by Charlson (1969) as the sum of several components:

$$(3) \quad b = b_{\text{scat}} + b_{\text{Rayleigh}} + b_{\text{abs-gas}} + b_{\text{abs-aerosol}}$$

where b_{scat} is the contribution due to light scattering by aerosol particles, b_{Rayleigh} is scattering due to air molecules, $b_{\text{abs-gas}}$ is light absorption due to gases like NO_2 , and $b_{\text{abs-aerosol}}$ represents absorption due to particles such as carbon black. Charlson, et al. (1972) observed that scattering usually dominates light extinction in the Los Angeles area atmosphere, with wavelength-dependent absorption by NO_2 being significant about 20 percent of the time.

While the theory of light scattering by aerosols is well advanced, there are practical difficulties in computing the effect of multicomponent smog aerosols on visibility from first principles in an urban situation. Extensive information would be needed on the size distribution of the aerosol, its refractive index, particle shape, illumination, humidification of the atmosphere, and the spatial

distribution of aerosol mass concentration. However, there is a growing body of empirical evidence suggesting that total suspended particulate mass concentration, TSP, alone is very highly correlated with scattering coefficient measurements and inversely correlated with prevailing visibility. From simultaneous measurements of light scattering and aerosol mass at a variety of locations, Charlson, Ahlquist and Horvath (1968) reported that:

$$(4) \quad L_V \cdot TSP \cong \frac{3.9 \text{ TSP}}{b} \cong 1.2 \frac{\text{gm}}{\text{m}^2}$$

or restated in units which we will use later:

$$(5) \quad b \cong 0.0325 \cdot (\text{TSP})$$

where b is the atmospheric extinction coefficient in units of $[10^4 \text{ m}]^{-1}$

TSP is the total suspended particulate mass in $\mu\text{gm}/\text{m}^3$

Visual range observations were correlated with aerosol mass loadings by Noll, Mueller and Imada (1968) and a similar proportionality was found.

Figure 1 shows a plot of the ratio of atmospheric light scattering coefficient to mass concentration for a monodisperse aerosol of unit density spherical particles of refractive index 1.5 and diameter D_p (White, Roberts and Friedlander, 1975). Much of the total suspended particulate mass in the atmosphere resides in a large particle mode ($D_p > 1\mu$) whose contribution to light scattering per unit mass concentration is well below that typically observed for the atmosphere as a whole; smaller particles of diameter equal to that of the wavelength of incoming solar radiation in the visible spectrum are the most effective light scatterers. This relatively small fraction of the particulate mass residing in the region around $D_p \cong 0.5$ microns is responsible for the bulk of the light scattering. *If these particles have an identifiable origin, then perhaps a relatively*

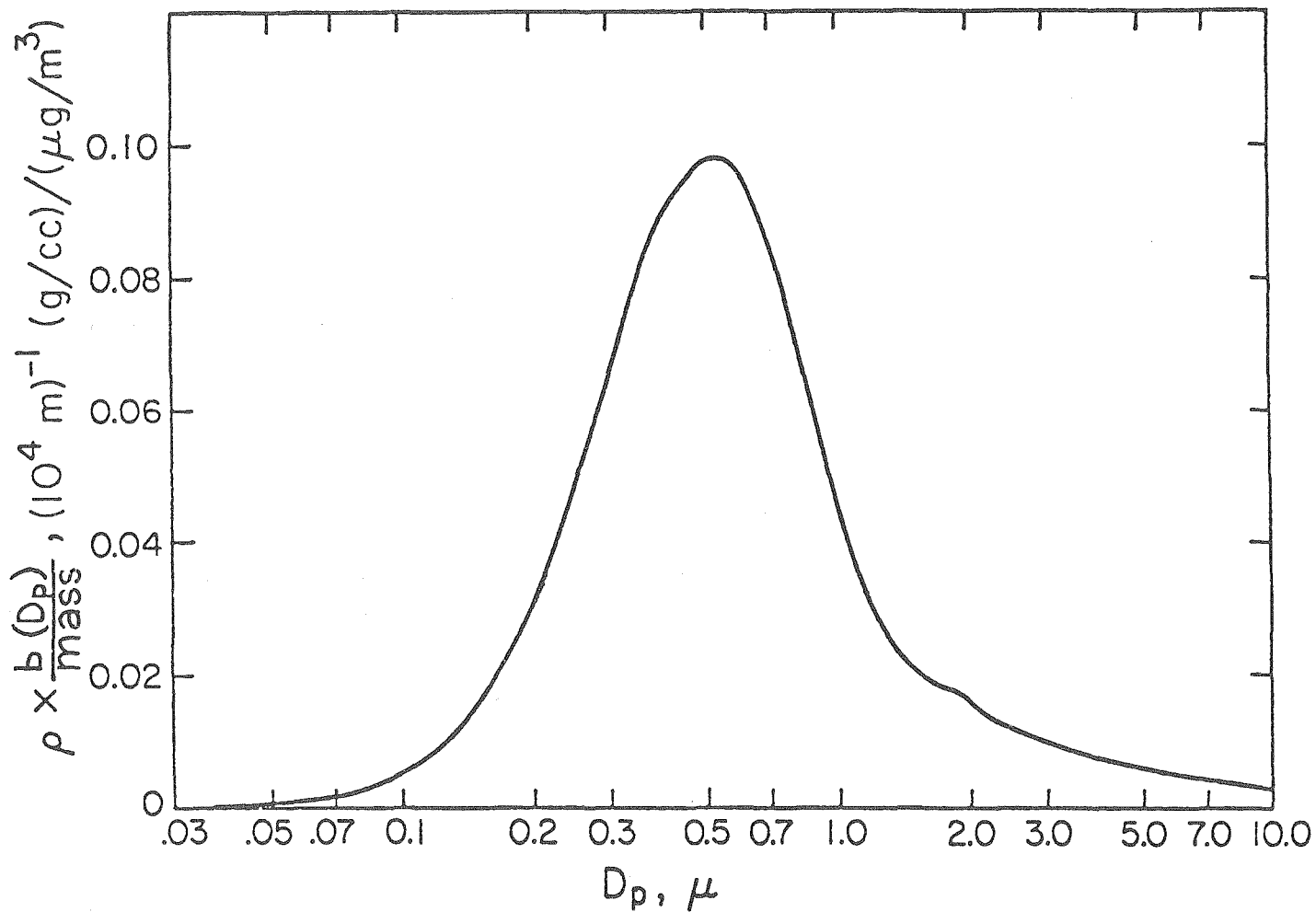


FIGURE 1 Normalized light scattering by aerosols as a function of particle diameter, D_p . Computed for unit density spherical particles of refractive index 1.5 (White,^p Roberts and Friedlander, 1975).

efficient strategy might be proposed for improving visibility in Los Angeles.

In a series of papers, Hidy and Friedlander and their co-workers (Hidy and Friedlander, 1971; Miller, Friedlander and Hidy, 1972; Heisler, Friedlander and Husar, 1973; Gartrell and Friedlander, 1975; Hidy et al., 1975) have examined the chemical composition of Los Angeles area atmospheric aerosols. These studies show that in Los Angeles the bulk of the particulate material in the effective light scattering size range (between one-tenth and one micron particle diameter) consists of sulfate, nitrate and ammonium ion, plus condensed organics. These portions of the atmospheric aerosol are known as secondary particulates because they originate predominantly from the conversion of pollutant gases to particulate matter in the atmosphere rather than from direct emission of dust or fume from natural or man-made sources.

The results of a variety of field investigations of visibility reduction support the proposition that such secondary particulates are largely responsible for atmospheric light extinction. Early studies of visibility reduction at Los Angeles, briefly outlined in Appendix I, make it clear that such a relationship has been understood at least qualitatively for a long time. The importance of secondary particulates to light scattering is hardly unique to downtown Los Angeles. Eggleton (1969), for example, found a close inverse relationship between ammonium sulfate concentration and visibility in England. Investigations by Lundgren (1970) demonstrated a strong inverse correlation between atmospheric nitrates and visibility at Riverside, California.

In an attempt to isolate the relative importance of various particulate species to light extinction, White and Roberts (1975) examined nine days of simultaneous observations on light scattering in relation to aerosol chemical composition in the Los Angeles area.

Their data consisted of 60 two-hour aerosol samples taken by the ACHEX II study (Hidy, et al., 1975) distributed among several locations in the Los Angeles basin along with nephelometer measurements of b_{scat} , plus relative humidity readings. They split the aerosol mass into four components: sulfates, nitrates, organics, and total mass less these three distinct chemical fractions. Postulating an additive relationship similar to expression (3), they were able to estimate the following dependence of b_{scat} on aerosol mass composition by linear regression techniques:

$$(6) \quad \frac{b_{\text{scat}}}{\text{TSP}} = 0.032 \pm 0.009$$

and

$$(7) \quad b_{\text{scat}} = 0.025 (\text{TSP-SULFATES-NITRATES}) \\ + 0.074 \text{ SULFATES} \\ + (0.025 + 0.049 \text{ RH}^2) \text{ NITRATES} - 1.1$$

$$R = 0.97 = \text{Multiple correlation coefficient}$$

where b_{scat} is in units of $[10^4 \text{ m}]^{-1}$

RH is relative humidity in (%/100)

TSP is total suspended particulate matter in micrograms per cubic meter

SULFATES and NITRATES are taken as $1.3 \cdot \text{SO}_4^{=}$ and $1.3 \cdot \text{NO}_3^-$ concentrations (in $\mu\text{gm}/\text{m}^3$) in order to account for the mass of associated cations (thought to be ammonium ion)

(TSP-SULFATES-NITRATES) thus denotes the non-sulfate, non-nitrate fraction of the total suspended particulate matter.

White and Roberts (1975) concluded that sulfates in the Los Angeles atmosphere are more effective light scatterers per unit mass than other suspended particulate components. Changes in relative humidity seemed to affect only light scattering by nitrates to a

statistically significant degree. Furthermore, light scattering by organics could not be distinguished statistically from the relatively ineffective scattering provided by the rest of the non-sulfate, non-nitrate, aerosol components, even though large amounts of organics were found to be present. The relative abundance of the various components of the atmospheric aerosols studied by White and Roberts is shown in Figure 2, while the estimated fraction of light scattering due to each component is shown in Figure 3 (White, Roberts and Friedlander, 1975).

From a knowledge of aerosol chemical composition, the emission source classes responsible for particulate concentrations at an air monitoring station may be inferred (Friedlander, 1973). Using trace metal concentrations at their monitoring sites as an indicator of pollutant origin, White, Roberts and Friedlander (1975) estimated that half of the light scattering at downtown Los Angeles was due to combustion of fuel oil and refining of crude oil. All but a few percent of the remaining light scattering at that location was attributed to pollutant emissions from automobiles.

An Investigation of Visibility in Relation to Atmospheric Composition at Downtown Los Angeles: 1965 through 1974

Our first objective is to determine whether the findings of White, Roberts and Friedlander are supported by the long-term historical particulate data base accumulated by the Los Angeles Air Pollution Control District (L.A. APCD). Ideally, one would like to be able to make comparisons between continuous records of particulate composition and visibility observations. A high degree of chemical and temporal resolution in the data base would be desired. The historical data base, however, was not designed with this particular experiment in mind. Total suspended particulate matter samples have been collected by the L.A. APCD at downtown Los Angeles by high volume sampling on a regular basis since August 1965. The sampling period is

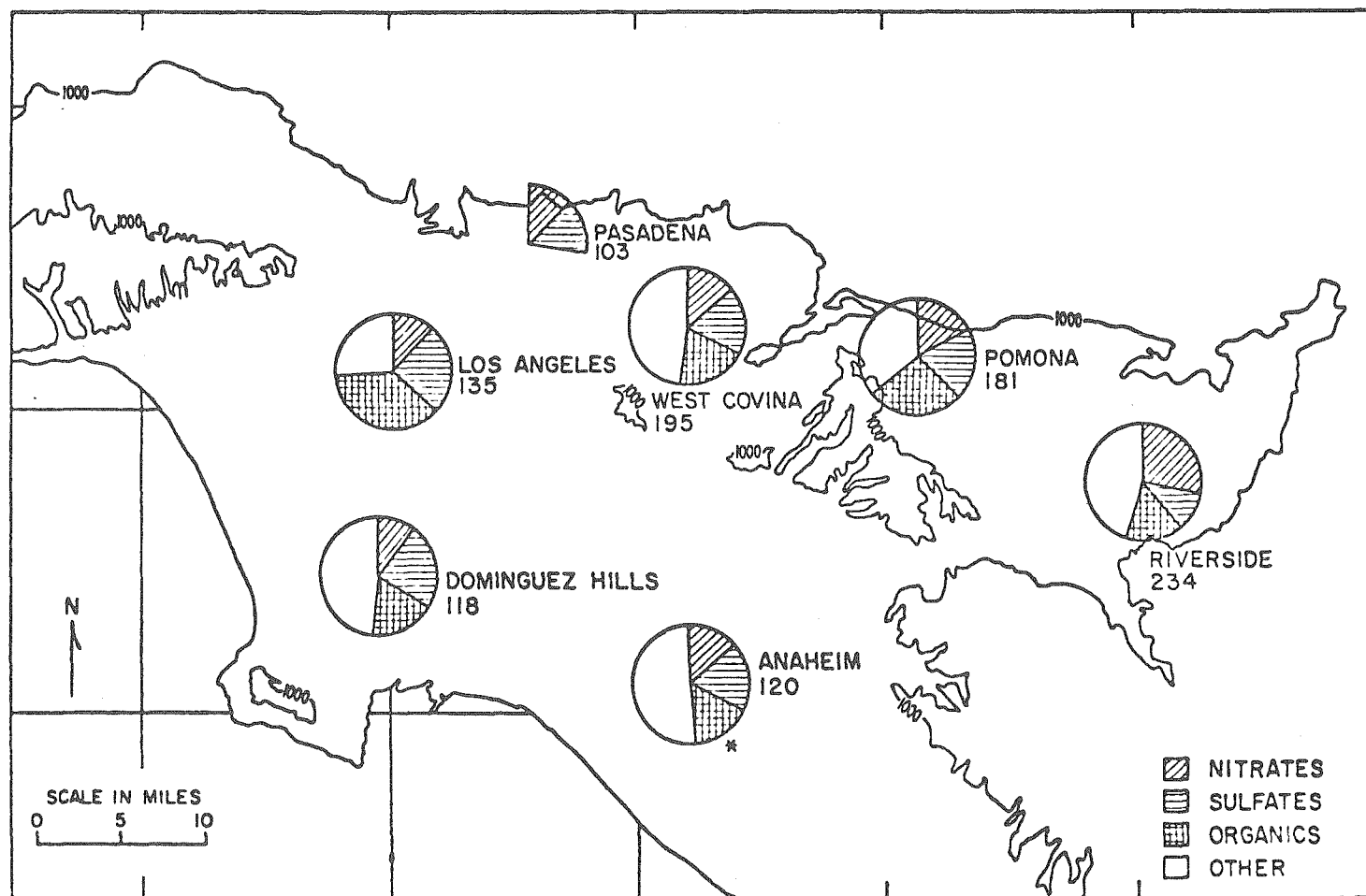


FIGURE 2 Division of total suspended particulate mass into its major chemical components on days and at locations covered by the ACHEX 1973 study. Numbers below locations give total suspended particulate mass in micrograms per cubic meter (from White, Roberts and Friedlander, 1975).

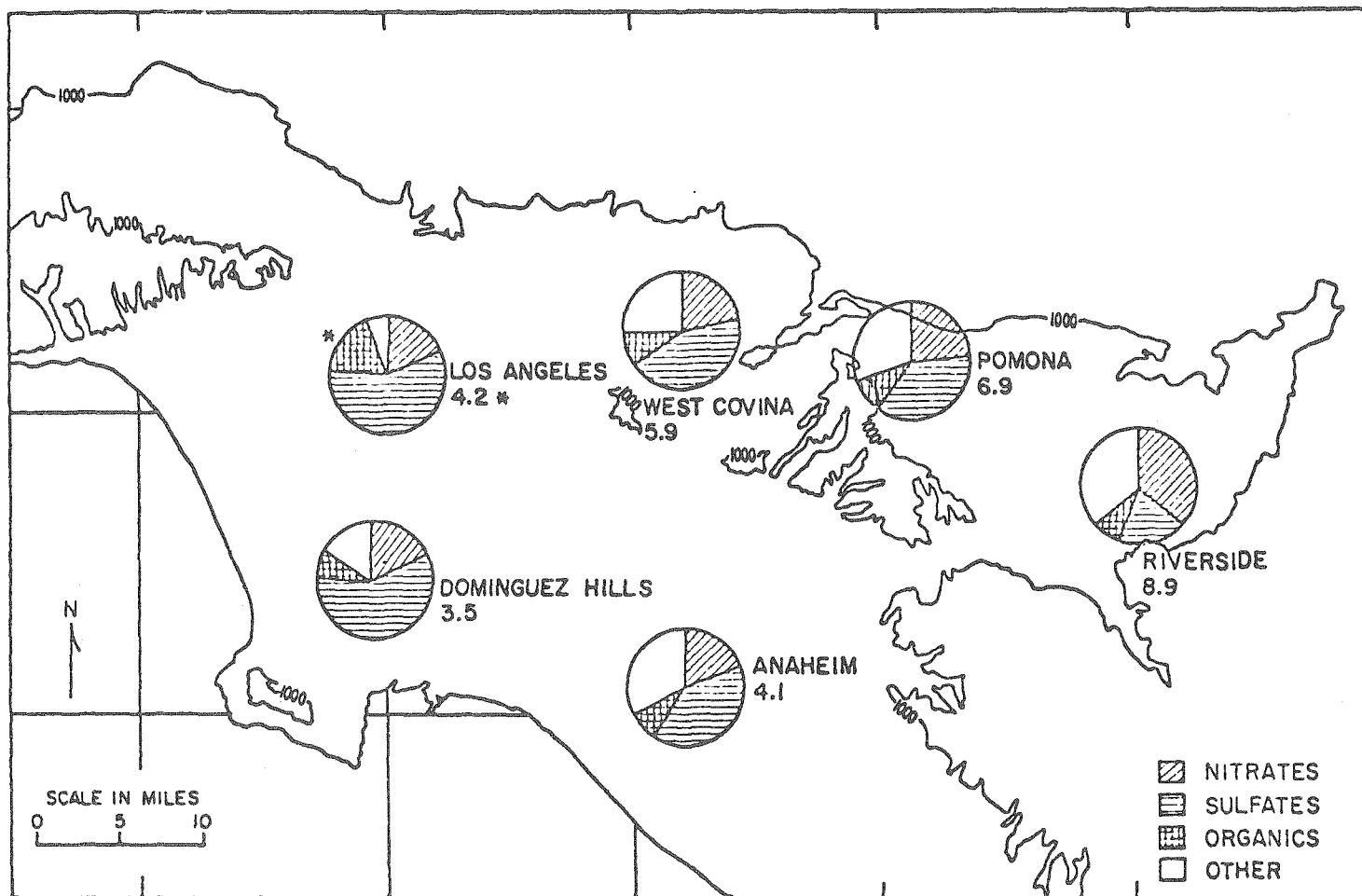


FIGURE 3 Attribution of b_{scat} to major components of the atmospheric aerosol at locations covered by the ACHEX 1973 study. Numbers below locations give average b_{scat} in units of $[10^4 \text{ m}]^{-1}$. Note the dominance of sulfates at downtown Los Angeles (from White, Roberts and Friedlander, 1975).

24 hours in duration. Duplicate samples are taken simultaneously on a pair of matched Staplex Hi Vols. Gravimetric determination of total suspended particulate matter collected is made after filter equilibration at low relative humidity. At least one sample taken from each pair of filters is analyzed for sulfates, nitrates, and seven metals. Sulfates are determined by the turbidimetric method and nitrates by the xylenol method. At various times during the history of the sampling program, sampling frequency has ranged from weekly, to twice weekly, to every fifth day. From August 1965 through August 1970, samples were taken from 8:00 a.m. to 8:00 a.m. Since that time, all samples were taken from midnight to midnight. The Air Pollution Control District's particulate sampling program is more fully described in a series of papers by MacPhee and Wadley (1972 through 1975).

Since July 1964, prevailing visibility observations have been taken at the downtown headquarters of the L.A. APCD. Observations are made from the roof of a building at 80 feet above ground level, at the same location and elevation as the high volume samplers. A typical daily record consists of nine consecutive hourly observations beginning at 8:00 a.m. civil time and ending at 4:00 p.m. civil time. Weekend observations are often not taken. Relative humidity data is available, usually for 14 daylight hours. Hourly observations on NO_2 concentrations (which could reduce visibility by absorption) have been taken at the same location by the automated continuous Saltzman method (Mills, Holland and Cherniack, 1974).

The temporal relationship between available useful observations is shown in Figure 4. There is clearly no way to adjust the historical data base to place 24-hour integrated particulate concentrations into exactly the same time frame as the daylight visibility observations. The best that can be done is to integrate the visibility observations for the longest period of time available within each particulate sampling event. Our mathematical treatment must take the available data into account. Suppose that we return to expression (3):

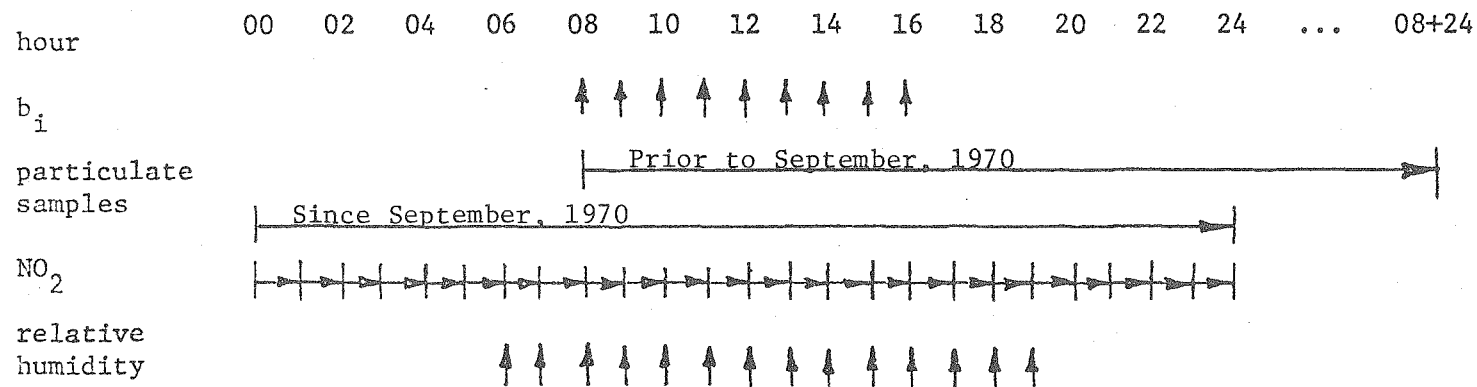


FIGURE 4 Temporal relationship between routine air monitoring observations. Averaging times indicated between arrows (\longleftrightarrow). Instantaneous readings indicated by (\uparrow).

$$(8) \quad b = b_{\text{scat}} + b_{\text{Rayleigh}} + b_{\text{abs-gas}} + b_{\text{abs-aerosol}}$$

Making the assumption that L_v equals prevailing visibility, V , at any instant, i , observations on the left hand side of (8) can be obtained from existing data by use of Koschmieder's formula as follows:

$$(9) \quad b_i \cong \frac{24.31}{V_i} \quad \text{for conversion of } V_i \text{ in miles to } b_i \text{ in } [10^4 \text{ meters}]^{-1}$$

where i now refers to the i^{th} hour of the day. After White and Roberts, we further assume that b_{scat_i} can be represented as the sum of the extinction contributions of distinct chemical subfractions of the measured particulate, plus associated water. Since prevailing visibility takes into account aerosol light extinction due to both scattering and absorption, we assume:

$$(10) \quad b_{\text{scat}_i} + b_{\text{abs-aerosol}_i} = \sum_m \beta_{m_i} M_{m_i}$$

where β_{m_i} = the extinction coefficient per unit mass of the m^{th} particulate chemical species at time i ;

M_{m_i} = the mass concentration of the m^{th} particulate chemical species at time i .

And similarly for light absorption by gases

$$(11) \quad b_{\text{abs-gas}_i} = \sum_n \gamma_{n_i} C_{n_i}$$

where γ_{n_i} = the extinction coefficient per unit volumetric concentration of the n^{th} gaseous chemical species at time i ;

C_{n_i} = the volumetric concentration of the n^{th} gaseous chemical species at time i .

Averaging over the t hours of visibility observations in a day, we obtain:

$$(12) \quad \frac{1}{t} \sum_{i=1}^t b_i = \frac{1}{t} \sum_{i=1}^t \sum_m \beta_{m_i} M_{m_i} + \frac{1}{t} \sum_{i=1}^t \sum_n \gamma_{n_i} C_{n_i} + b_{\text{Rayleigh}},$$

where b_{Rayleigh} is taken as constant. Let \bar{M}_m be the available 24-hour average concentration of particulate species m . Let M_{m_i} be decomposed into the sum of a 24-hour mean value plus a fluctuating component:

$$(13) \quad \beta_{m_i} M_{m_i} = \beta_{m_i} (\bar{M}_m + M'_{m_i})$$

Forming a t hour daylight average corresponding to our period of visibility observations, and rearranging:

$$(14) \quad \frac{1}{t} \sum_{i=1}^t \beta_{m_i} M_{m_i} = \frac{1}{t} \sum_{i=1}^t \beta_{m_i} \bar{M}_m + \frac{1}{t} \sum_{i=1}^t \beta_{m_i} M'_{m_i}$$

For ease of notation, the last term on the right side of expression (14) will be referred to as δ_m , the daily residual difference between the average of $\beta_m M_m$ and the product of the separate averages of β_m and M_m . Summing (14) over the particulate species and assuming that light absorption per unit concentration by pollutant gases is unchanging over time, we may substitute into (12) and rearrange to get

$$(15) \quad \bar{b} = \frac{1}{t} \sum_{i=1}^t b_i = \sum_m \frac{1}{t} \sum_{i=1}^t \beta_{m_i} \bar{M}_m + \sum_n \gamma_n \frac{1}{t} \sum_{i=1}^t C_{n_i} + b_{\text{Rayleigh}} + \sum_m \delta_m$$

The Models Estimated

Following the practice of previous investigators, and as a rough check on the visibility and total suspended particulate data (TSP), a purely linear relationship will be fit between undifferentiated aerosol mass and light extinction similar to equation (6):

$$(16) \quad \bar{b}_j = \beta_{\text{TSP}} \cdot \text{TSP}_j + \alpha \cdot \text{DUMMY}_j + A + \epsilon_j$$

As used above, \bar{b}_j is the average extinction coefficient for t hours of visibility data (nominally $t = 9$) on any day, j , as estimated from prevailing visibility by Koschmieder's formula. Only a single particulate species is considered, and light extinction per unit particulate concentration, β_{TSP} , is taken as an undertermined constant. Light

absorption by gases is neglected. In this model and those that follow, a dummy variable, $DUMMY_j$, has been introduced to capture any effect on equation fit due to the change in particulate sampling schedule previously noted to have occurred beginning in September 1970. $DUMMY_j$ will be taken as unity for all samples prior to September 1970, and zero for all samples taken thereafter. The term $b_{Rayleigh}$ is absorbed into the regression constant, A , in equation (16). For the time being we will assume that the residual difference term $\sum_m \delta_m$ from equation (15) has mean zero and random fluctuation about its mean, and thus will be absorbed into the daily residual, ϵ_j . This assumption is not likely to be strictly correct, as will be discussed later.

Results of the regression of extinction coefficient on total suspended particulate concentration alone are shown in Table I.¹ Referring to the second entry of Table I, we see that the estimated light scattering coefficient per unit total suspended particulate concentration is virtually identical to that found by the short-term study of White and Roberts (1975), as shown in equation (6). The coefficient β_{TSP} is significantly different from zero with greater than 99 percent confidence, while the constant term, A , was not significantly different from zero at any reasonable confidence level. However, the total fit of the model, as judged by the reduction in residual variance, is unimpressive. Twenty-four hour total suspended particulate concentration values alone are not a very precise estimator of daylight visibility reduction in the Los Angeles area.

Next, by analogy to equation (15), a series of regression models are proposed to explain the average light extinction coefficient, \bar{b}_j ,

¹ All computations shown in Tables I and II were performed using the double precision ordinary least squares stepwise regression package of the MAGIC data handling program maintained on the Caltech IBM 370/158 computer by R. C. Y. Koh. Data base preparation is detailed in Appendix II, along with a statistical description of the data used.

TABLE I

$$\text{Model Estimated: } \bar{b}_j = \beta_{\text{TSP}} \cdot \text{TSP}_j + \alpha \cdot \text{DUMMY}_j + A + \varepsilon_j$$

Entry Number	Time Period	Number of Observations	\bar{b}_j (\bar{b}_j Variance)	β_{TSP}	Coefficients (Standard Error)		Correlation Coefficient (Variance of Residual)
					α	A	
1.	8/65 thru 12/74	413	6.62 (30.52)	0.037 (0.0043)	1.023 (0.498)	0.154 NS	0.40 (25.53)
2.	9/70 thru 12/74	199	6.01 (18.19)	0.032 (0.0044)	N/A	1.034 NS	0.45 (14.41)

Legend: N/A means that the dummy variable is not applicable in a regression involving only data taken after the change in particulate sampling schedule.

NS means not significantly different from zero at a 95% confidence level.

on any day j at downtown Los Angeles as a detailed function of atmospheric composition. These models differ only in the means of incorporating relative humidity effects into the structure of the model.

Of necessity, in light of the available data, it is assumed that division of the particulate samples into SULFATES, NITRATES, and (TSP-SULFATES-NITRATES) is sufficient to capture the major light scattering differences between these particulate components which can be resolved on the basis of chemical analysis. It is further assumed that NO_2 is the only light absorbing gas of major significance to light extinction in the Los Angeles Basin.

Incorporation of relative humidity into our model poses several potentially serious problems. As relative humidity rises, hygroscopic and deliquescent particles pick up associated water and grow in size. Usually, this humidity-induced growth of an atmospheric aerosol is accompanied by an increase in light scattering which is not necessarily linear in relative humidity.² Three different approaches will be tried in an attempt to deal with the relative humidity effect.

In the first case, a baseline for comparison of relative humidity-dependent models is established. The suspected non-linearity is disregarded, and a purely linear model is proposed:

$$\begin{aligned}
 (17) \quad \bar{b}_j = & \beta_{\text{SULFATES}} \cdot \text{SULFATES}_j + \beta_{\text{NITRATES}} \cdot \text{NITRATES}_j \\
 & + \beta_{(\text{TSP-SULFATES-NITRATES})} \cdot (\text{TSP-SULFATES-NITRATES})_j \\
 & + \gamma_{\text{NO}_2} \cdot \overline{\text{NO}_2}_j + \Delta_{\text{RH}} \cdot \overline{\text{RH}}_j + \alpha \cdot \text{DUMMY}_j + A + \epsilon_j.
 \end{aligned}$$

In this simple model, the light scattering coefficients per unit concentration, β_m and γ_{NO_2} , are taken to be undetermined constants, and the difference between light extinction on a high vs. low humidity day is captured by the undetermined coefficient, Δ_{RH} , applied to the daytime average relative humidity.

²Growth associated with increased humidification may also affect atmospheric chemistry, for example, by providing a larger volume of the solution phase as a site for liquid phase reactions.

When the chemically resolved linear model of equation (17) is estimated for the entire range of available average relative humidities (Table II, entries 1 and 2), a substantial improvement in explanatory power is achieved over the total suspended particulate model of equation (16). Sulfates and NO_2 are implicated as major contributors to visibility reduction at downtown Los Angeles. As expected, increasing relative humidity is related to increasing light extinction, as shown by the significant t test on the coefficient Δ_{RH} . The estimated light extinction coefficients per unit concentration for NITRATES and (TSP-SULFATES-NITRATES) are at least an order of magnitude lower than that for SULFATES. In the case of NITRATES, the coefficient is not significantly different from zero at any reasonable confidence level for either time grouping tested. The constant term, A, is significantly less than zero in all years tested. This is not too surprising since an attempt to fit a linear function to a non-linear phenomenon will likely result in the numerous days of high light extinction at higher relative humidities dominating the location of the intercept, rather than the few days of extremely good visibility which should fall close to the origin of our coordinate system.

Upon examination of the extinction coefficient data, it was observed that roughly half of the variance of \bar{b}_j was contributed by a few very high values from among the 413 available samples. For example, on January 21, 1970, prevailing visibility ranged from 0.2 miles to 0.8 miles during the day, while relative humidity for the daylight hours averaged 87 percent, indicating a high likelihood of stabilized fog. The effect of deleting such observations from the data base was investigated. Discarding the data for all seven days over the nine-year period for which \bar{b}_j exceeded $20 \times [10^4 \text{ m}]^{-1}$, then re-estimating the previous model, the results shown in entry 3 of Table II are obtained. The coefficients in this model are similar to those of entry 2 of Table II which employed all of the data available since the change in sampling schedule in August of 1970. All coefficients except β_{NITRATES}

TABLE II

MODEL ESTIMATED:

$$\bar{b}_j = \beta_{\text{SULFATES}} \cdot \text{SULFATES}_j + \beta_{\text{NITRATES}} \cdot \text{NITRATES}_j + \beta_{(\text{TSP-SULFATES-NITRATES})} \cdot (\text{TSP-SULFATES-NITRATES})_j + \gamma_{\text{NO}_2} \cdot \overline{\text{NO}_2}_j + \Delta_{\text{RH}} \cdot \overline{\text{RH}}_j + \alpha \cdot \text{DUMMY}_j + A + \epsilon_j$$

ENTRY NO.	TIME PERIOD	NUMBER OF USABLE OBSERVATIONS (Comments)	\bar{b}_j Average (\bar{b}_j Variance)	β_{SULFATES}	β_{NITRATES}	COEFFICIENTS (Standard Error) $\beta_{(\text{TSP-SULFATES-NITRATES})}$	γ_{NO_2}	Δ_{RH}	α	A	Correlation Coef. (Variance of Residual)
1.	8/65 thru 12/74	413	6.62 (30.52)	0.173 (0.015)	0.014 (0.019) NS	0.0080 (0.0043) S ₉₀	38.30 (4.42)	8.30 (1.27)	2.89 (0.38)	-7.37 (0.93)	0.76 (12.70)
2.	9/70 thru 12/74	199	6.01 (18.19)	0.161 (0.012)	-0.016 (0.013) NS	0.0080 (0.0034)	29.79 (3.69)	4.33 (1.22)	N/A	-3.53 (0.84)	0.86 (4.62)
3.	8/65 thru 12/74	406 (seven observations with $b_j > 20$ removed)	6.20 (15.84)	0.157 (0.009)	-0.017 (0.011) NS	0.0152 (0.0026)	24.99 (2.66)	6.36 (0.76)	1.85 (0.23)	-4.98 (0.56)	0.85 (4.35)
4.	8/65 thru 12/74	390 (visibility data used only when RH not > 70%)	5.65 (14.68)	0.134 (0.0096)	-0.0063 (0.0116) NS	0.013 (0.0026)	28.57 (2.63)	6.14 (0.95)	1.79 (0.24)	-4.84 (0.61)	0.82 (4.63)
5.	9/70 thru 12/74	192 (visibility data used only when RH not > 70%)	5.18 (13.08)	0.139 (0.011)	-0.0098 (0.0115) NS	0.0040 (0.0030) NS	29.17 (3.05)	2.78 (1.28)	N/A	-2.13 (0.76)	0.86 (3.39)

Legend: All coefficients are significantly different from zero with greater than 95% confidence unless otherwise indicated.

NS means not significantly different from zero at a 95% confidence level.

S₉₀ means significantly different from zero with greater than 90% confidence.

N/A means that the dummy variable is not applicable in a regression involving only data taken after the change in particulate sampling schedule.

are significantly different from zero with greater than 99 percent confidence. The t statistic on β_{SULFATES} is very large.

The second approach taken to dealing with the relative humidity effect is to attempt to remove the non-linearity by selecting only those observations which occur at low relative humidity. Equation (17) will again be the basis for the model, but this time daily visibility, humidity, and NO_2 averages will be computed only for those hours in the day for which relative humidity was not greater than 70 percent. Data for days of persistent high humidity will be discarded.

When the chemically resolved linear model of equation (17) is applied to the low humidity data base, the relationships outlined in Table II entries 4 and 5 are found. The size of the relative humidity effect has been reduced, but not eliminated, as shown by comparison of Δ_{RH} between corresponding entries 1 and 4, as well as between entries 2 and 5 of Table II. The size of the coefficient β_{SULFATES} has been reduced to a lower value of between 0.139 and 0.134 $[10^4 \text{ m}]^{-1}$ per $\mu\text{gm}/\text{m}^3$ when the higher humidity observations are eliminated, a trend which was not unexpected. The fit of the low humidity model is comparable to that obtained in the regressions of entries 2 and 3 of Table II.

A third model which attempts to deal directly with the physical basis of the relative humidity effect is proposed as follows. The radius of a hygroscopic particle in equilibrium with a surrounding humid atmosphere is determined by a competition between the vapor pressure raising effects of particle surface curvature and the vapor pressure lowering effect of dissolved substances in the particle. Neiburger and Wurtele (1949) used this fact to develop a model for correlating light scattering with relative humidity over a broad range of relative humidities. Their analysis shows that particle radius, r_p , should as a rough approximation be dependent on solute mass, m_s , and relative humidity as follows:

$$(18) \quad r_p = K[m_s / (1-RH)]^{1/3}$$

where K is a parameter of the dissolved substance which is approximately constant over a broad range of temperature and solute concentration. Approximation of changes in particle size by a hyperbolic function of relative humidity, though not strictly correct, provides a practical basis for non-linear regression analysis without introducing an excessive number of degrees of freedom into the curve-fitting processes. A brief summary of Neiburger and Wurtele's derivation is contained in Appendix III.

Neiburger and Wurtele were concerned with large sea salt particles of several microns in diameter. They noted that for a given particle number concentration and solute mass per particle, light scattering by large particles should increase as the cross-sectional area of the aerosol, and thus light scattering should be correlated with relative humidity as $(1-RH)^{-2/3}$. Our case of interest is considerably more complicated than Neiburger and Wurtele's hypothetical behavior of uniform sea salt solution droplets. As previously mentioned, the bulk of the soluble salts in the atmosphere at downtown Los Angeles are thought to consist of sulfate and nitrate compounds. These particles are found predominantly in submicron size ranges where the Mie theory of light scattering would not predict a simple dependence of light scattering on particle cross-sectional area as was the case with Neiburger and Wurtele's larger sea salt nuclei. However, Hidy, et al. (1975) have shown empirically that light scattering by submicron aerosols is well correlated with total submicron aerosol volume. Thus it is expected that light scattering by a hygroscopic submicron aerosol will correlate well with changes in particle radius cubed. If it is assumed that total suspended solute mass concentration changes from day to day are proportional to changes in total particle number concentration, with the relative shape of the size distribution of dry solute nuclei remaining unchanged from day to day, then light scattering by SULFATES and

NITRATES might be fit by a regression model containing the terms $\beta_{SO_4} \cdot (1-RH)^{-1} \cdot \text{SULFATES}$ and $\beta_{NO_3} \cdot (1-RH)^{-1} \cdot \text{NITRATES}$.

Treatment of the effect of relative humidity on the non-SULFATE, non-NITRATE portion of the total suspended particulate matter is complicated by lack of detailed information on its chemical composition. Much of the remaining particulate mass is thought to reside in larger size ranges where light scattering per particle should be proportional to particle cross-sectional area. If the particles were hygroscopic, then a dependence of light scattering on relative humidity of $(1-RH)^{-2/3}$ would be indicated, similar to Neiburger and Wurtele's sea salt droplets. If the particles are hydrophobic, then no dependence on relative humidity is expected, and the term $(1-RH)$ would be raised to the zero power. In all likelihood, the atmospheric aerosol contains a mix of both types of large particles, and thus some intermediate behavior would be found to represent the relative humidity dependence of best fit. Therefore, our third regression model will be formulated as:

$$(19) \quad \bar{b}_j = \beta_{SO_4} \cdot \left(\frac{1}{t} \sum_{i=1}^t (1-RH_i)^{\Delta_{SO_4}} \right)_j \cdot \text{SULFATES}_j + \beta_{NO_3} \cdot \left(\frac{1}{t} \sum_{i=1}^t (1-RH_i)^{\Delta_{NO_3}} \right)_j \cdot \text{NITRATES}_j \\ + \beta_{(TSP-SULFATES-NITRATES)} \cdot \left(\frac{1}{t} \sum_{i=1}^t (1-RH_i)^{\Delta_P} \right)_j \cdot (TSP-SULFATES-NITRATES)_j \\ + \gamma_{NO_2} \cdot \overline{NO_2}_j + \alpha \cdot \text{DUMMY}_j + A + \epsilon_j$$

where each symbol is as previously defined, except that the Δ_m are now undetermined exponents applied to the relative humidity dependence of light scattering by aerosol species m.

The non-linear model of equation (19) is not suitable to fitting by ordinary least squares regression procedures. Therefore the results of Table III were obtained by minimizing the sum of the squared residuals by the algorithm suggested by Marquardt (1963) as implemented by the Caltech computing center subroutine LSQENP.

Entry 1 of Table III begins with a test of our prior beliefs about the relative humidity dependence of light scattering by various

TABLE III

MODEL ESTIMATED:

$$\bar{b}_j = \beta_{SO_4} \cdot \left(\frac{1}{t} \sum_{i=1}^t (1-RH_i) \Delta_{SO_4} \right)_j \cdot \text{SULFATES}_j + \beta_{NO_3} \cdot \left(\frac{1}{t} \sum_{i=1}^t (1-RH_i) \Delta_{NO_3} \right)_j \cdot \text{NITRATES}_j + \beta_{(TSP-SULFATES-NITRATES)} \cdot \left(\frac{1}{t} \sum_{i=1}^t (1-RH_i) \Delta_p \right)_j \cdot (TSP-SULFATES-NITRATES)_j + \gamma_{NO_2} \cdot \overline{NO_2}_j + \alpha \cdot \text{DUMMY}_j + A + \epsilon_j$$

TIME PERIOD: August 1965 through December 1974

NUMBER OF USABLE OBSERVATIONS = 413

ENTRY NO.	COMMENTS	\bar{b}_j (b_j Variance)	Average β_{SO_4}	Δ_{SO_4}	β_{NO_3}	Δ_{NO_3}	COEFFICIENTS (Standard Error)		γ_{NO_2}	α	A	CORRELATION COEF. (Variance of Residual)
							β (TSP-SULFATES -NITRATES)	Δ_P				
1.	Δ_{SO_4} and Δ_{NO_3} forced to equal -1.0 Δ_P forced to equal -0.667	6.62 (30.53)	0.041 (0.003)	-1.0 Fixed	0.025 (0.005)	-1.0 Fixed	-0.002 (0.002) NS	-0.667 Fixed	41.80 (3.86)	2.54 (0.38)	-1.76 (0.51)	0.76 (13.03)
2.	Δ_{SO_4} and Δ_{NO_3} forced to equal -1.0	6.62 (30.53)	0.039 (0.004)	-1.0 Fixed	0.022 (0.005)	-1.0 Fixed	0.004 (0.005) NS	-0.24 (0.96) NS	38.57 (4.43)	2.31 (0.38)	-2.23 (0.56)	0.76 (13.02)
3.	Δ_{SO_4} forced to equal Δ_{NO_3}	6.62 (30.53)	0.089 (0.010)	-0.67 (0.077)	0.040 (0.0095)	-0.67 (0.077)	0.0038 (0.0047) NS	-0.35 (0.92) NS	33.81 (4.14)	2.87 (0.36)	-3.28 (0.54)	0.80 (11.13)
4.	All parameters free to seek local minimum	6.62 (30.53)	0.107 (0.015)	-0.53 (0.10)	0.024 (0.008)	-1.09 (0.13)	0.0033 (0.0046) NS	-0.28 (1.07) NS	33.86 (4.07)	2.82 (0.35)	-3.14 (0.53)	0.81 (10.68)

Legend: NS means not significantly different from zero at a 95% confidence level.

types of aerosol species. The exponents Δ_{SO_4} and Δ_{NO_3} are initially set equal to -1.0 reflecting the expected correlation between submicron aerosol volume and light scattering. The exponent Δ_p is first set equal to -0.667 as would be the case if total suspended particulate matter resided in large particles which could grow in size with increasing humidification. The fit achieved is comparable to that of the linear model of entry 1, Table II fitted to the same data base. The only coefficient which is not of the expected sign appears to be insignificantly different from zero. The principal species responsible for explaining visibility reduction are again SULFATES and NO_2 . The light extinction coefficient estimated for NO_2 is similar to that of entry 1, Table II, indicating that our change in humidity treatment has left estimated light attenuation by this gas phase component largely unaffected, as expected. Finally, we note that the change in relative humidity treatment has brought the intercept, A, closer to zero, and for the period prior to September 1970 the coefficient on the dummy variable, α , almost cancels A, leaving a net intercept value which is indistinguishable from zero. In short, our model based on simple assumptions about the light scattering behavior of a hygroscopic aerosol as a function of relative humidity displays many nice properties.

In an attempt to improve model fit, constraints placed on the exponents describing the relative humidity dependence of light scattering by various aerosol components will be relaxed one at a time. Perturbation of the parameter values shows that there is roughly a one-to-one trade-off possible between the values of the coefficients β_{SO_4} and Δ_{SO_4} without disturbing model fit very much. Similar compensating adjustments could be made between β_{NO_3} and Δ_{NO_3} and between $\beta_{(TSP-SULFATES-NITRATES)}$ and Δ_p . Total model fit continues to improve until all parameters Δ_m are freed to seek a local minimum in entry 4 of Table III. In that case, the function of relative humidity associated with NITRATES almost exactly matches our prior expectation that Δ_{NO_3} would equal -1.0. Light scattering by SULFATES is also a fairly

strong function of relative humidity. Coefficients estimating the light scattering by non-sulfate non-nitrate particulates are now of the expected sign, but are still not known with great accuracy.

Figure 5 shows the historical cumulative distribution of visibilities at downtown Los Angeles as compared to model output of entry 4, Table III. The comparison is quite close.

Theoretical calculations have been performed by Garland (1969) to determine the extinction coefficient per unit concentration for liquid phase atmospheric ammonium sulfate aerosols as a function of relative humidity. Garland's example calculation for light scattering by a monodisperse ammonium sulfate aerosol of dry particle diameter equal to 0.42μ is plotted in Figure 6 along with the values of the function $\beta_{\text{SULFATES}} = \beta_{\text{SO}_4} (1-\text{RH})^{\Delta\text{SO}_4}$ from entry 4 of Table III. The regression results are of similar shape, but somewhat higher than Garland's extinction coefficient calculations. If the assumption were made that the sulfate aerosols in Los Angeles over the period 1965 through 1974 on days of high relative humidity were predominantly ammonium sulfate, then the comparison would be somewhat closer. That is because the molecular weight of ammonium sulfate is 1.38 times that of the $\text{SO}_4^{=}$ ion, instead of the 1.3 times greater proportionality assumed at our data preparation step.

The model of equation (19) has the great advantage that it is close to being physically realizable for a hygroscopic aerosol. However, many sulfate and nitrate species exhibit a pronounced deliquescence. For example, light scattering by ammonium sulfate particles is not a smooth, slowly increasing function of relative humidity over a broad range of humidification. Instead, light scattering per unit mass for an ammonium sulfate aerosol remains fairly constant up to a relative humidity of ca. 80 percent, at which point the particle goes rapidly into solution with an attendant sharp rise in light scattering (Charlson, et al., 1974). Such complicated behavior would be difficult

COMPARISON OF HISTORIC DISTRIBUTION OF VISIBILITIES AT LOS ANGELES (SOLID LINE)

VS. VISIBILITY DISTRIBUTION SYNTHESIZED FROM FITTED MODEL OF EQ.19 (+'S)

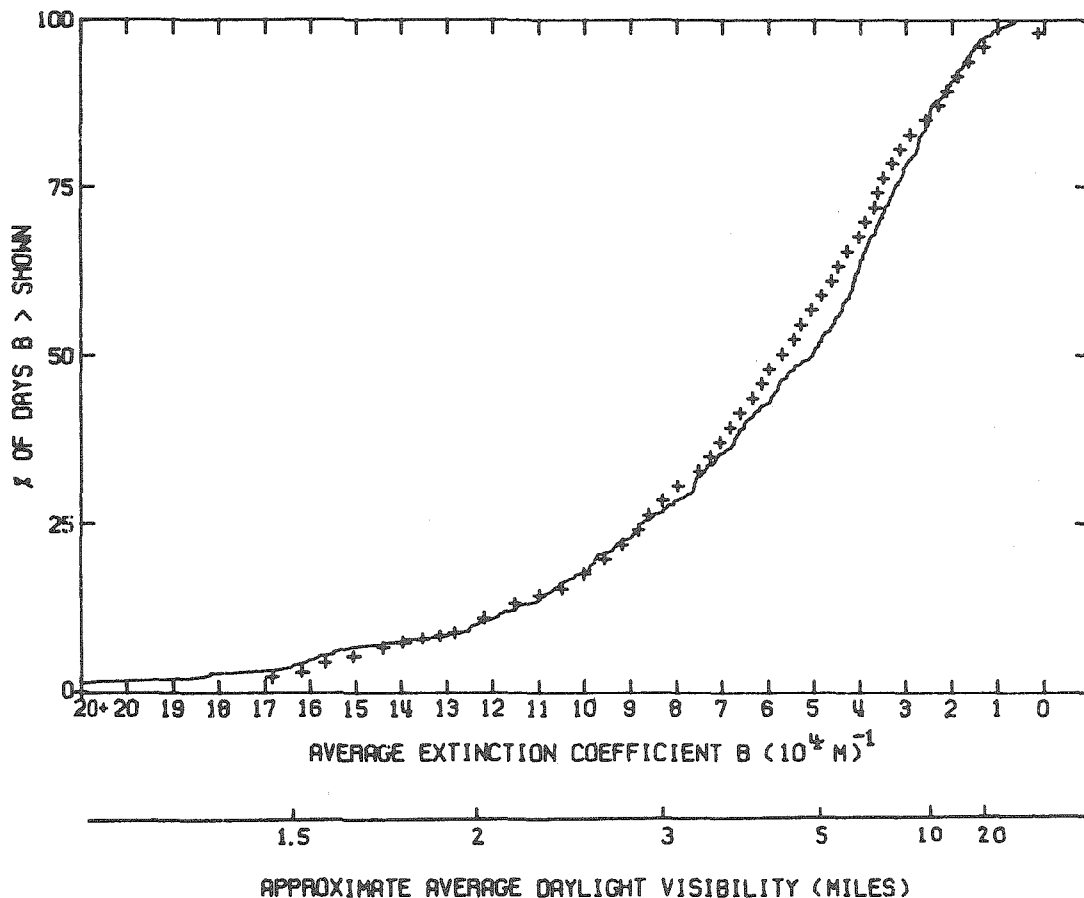


FIGURE 5 Results of model of entry 4, Table III. Cumulative distribution of days on which the average extinction coefficient, \bar{b}_j , exceeded the stated values during the period August 1965 to December 1974 (413 days considered). Solid curve is historic data from L.A. APCD visibility measurements. Broken curve is synthesized from regression model shown in entry 4 of Table III.

LIGHT SCATTERING BY SULFATES AS A FUNCTION OF RELATIVE HUMIDITY

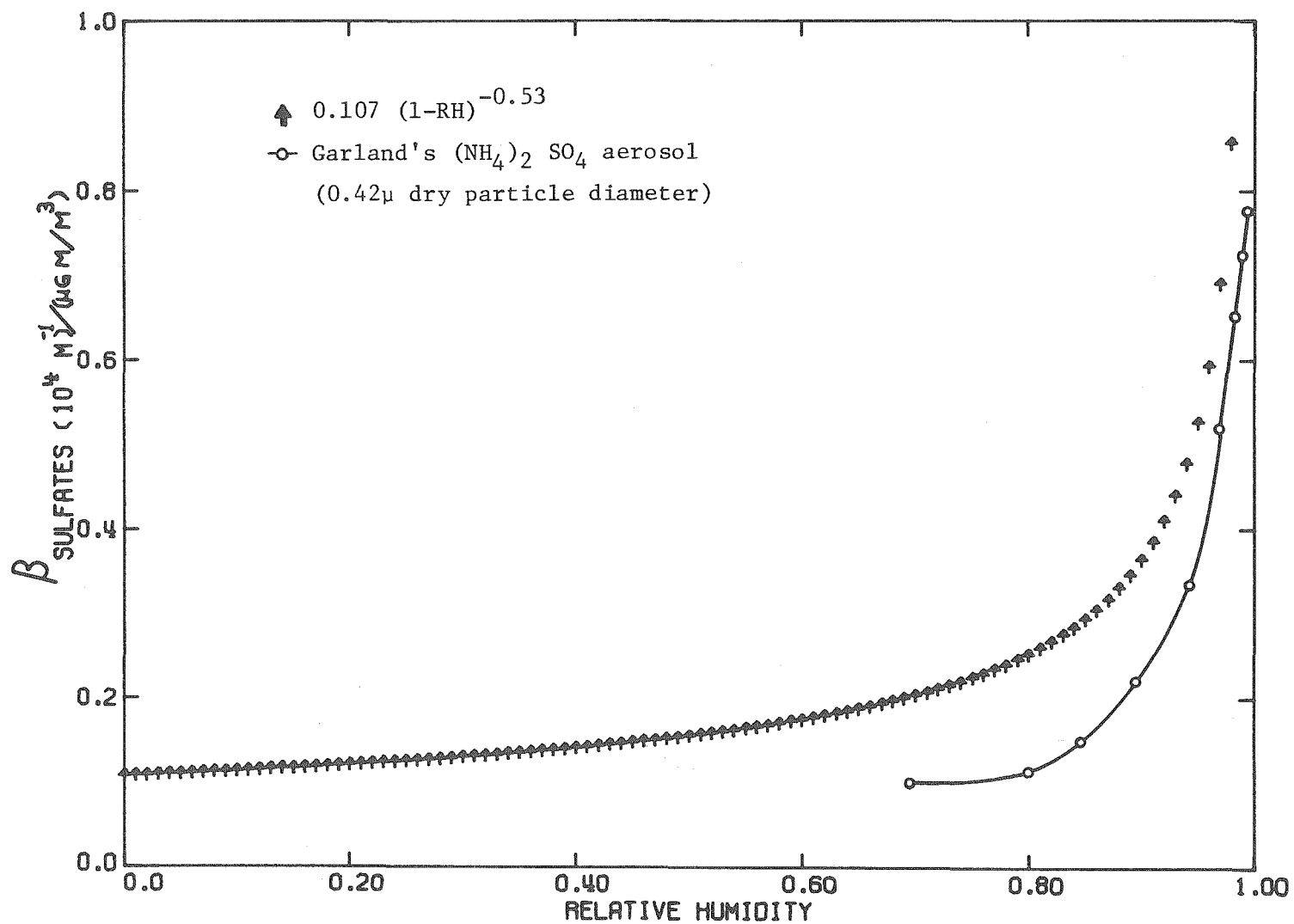


FIGURE 6

to incorporate theoretically into a simple regression model. Instead, an approach similar to that adopted by White and Roberts (1975) was tested in which an arbitrary relative humidity effect was to be approximated by fitting coefficients to series constructed from polynomials in relative humidity, pre-multiplying each aerosol mass concentration term. That approach was abandoned after discovering that only a slight improvement in model fit was achieved at the expense of creating estimated light scattering functions for each aerosol species which were ill-behaved at either the highest or lowest ends of the possible relative humidity range.

The function $\beta_{\text{NITRATES}} = \beta_{\text{NO}_3} (1-\text{RH})^{\Delta_{\text{NO}_3}}$ describing light scattering by NITRATES as a function of relative humidity from entry 4 of Table III is plotted in Figure 7. Also plotted is the function $(0.025 + 0.049 \text{ RH}^2)$ from equation (7) describing White and Roberts' result for light scattering by NITRATES. At relative humidities below 60 percent, our estimate matches that of White and Roberts almost exactly.

In the regression models tested, the estimated light extinction coefficient per ppm for NO_2 has ranged between $41.80 [10^4 \text{ m}]^{-1}$ and $24.99 [10^4 \text{ m}]^{-1}$. In all but one case, the estimate of γ_{NO_2} is within two standard errors of $30 [10^4 \text{ m}]^{-1}$ per ppm. That value exceeds the literature estimates for light absorption by NO_2 as cited by Charlson and Ahlquist (1969) by roughly a factor of two to four, depending on the wavelength of light of interest. The discrepancy could be due in part to systematic underestimation of either NO_2 concentration or overestimation of the total atmospheric extinction coefficient. From the comments of previous investigators, it is not at all unlikely that less than ideal availability of visibility markers, plus the requirement that the markers be clearly recognized and not just seen could lead to a minimum contrast level for prevailing visibility observations in Los Angeles of 0.05 instead of Koschmieder's value

LIGHT SCATTERING BY NITRATES AS A FUNCTION OF RELATIVE HUMIDITY

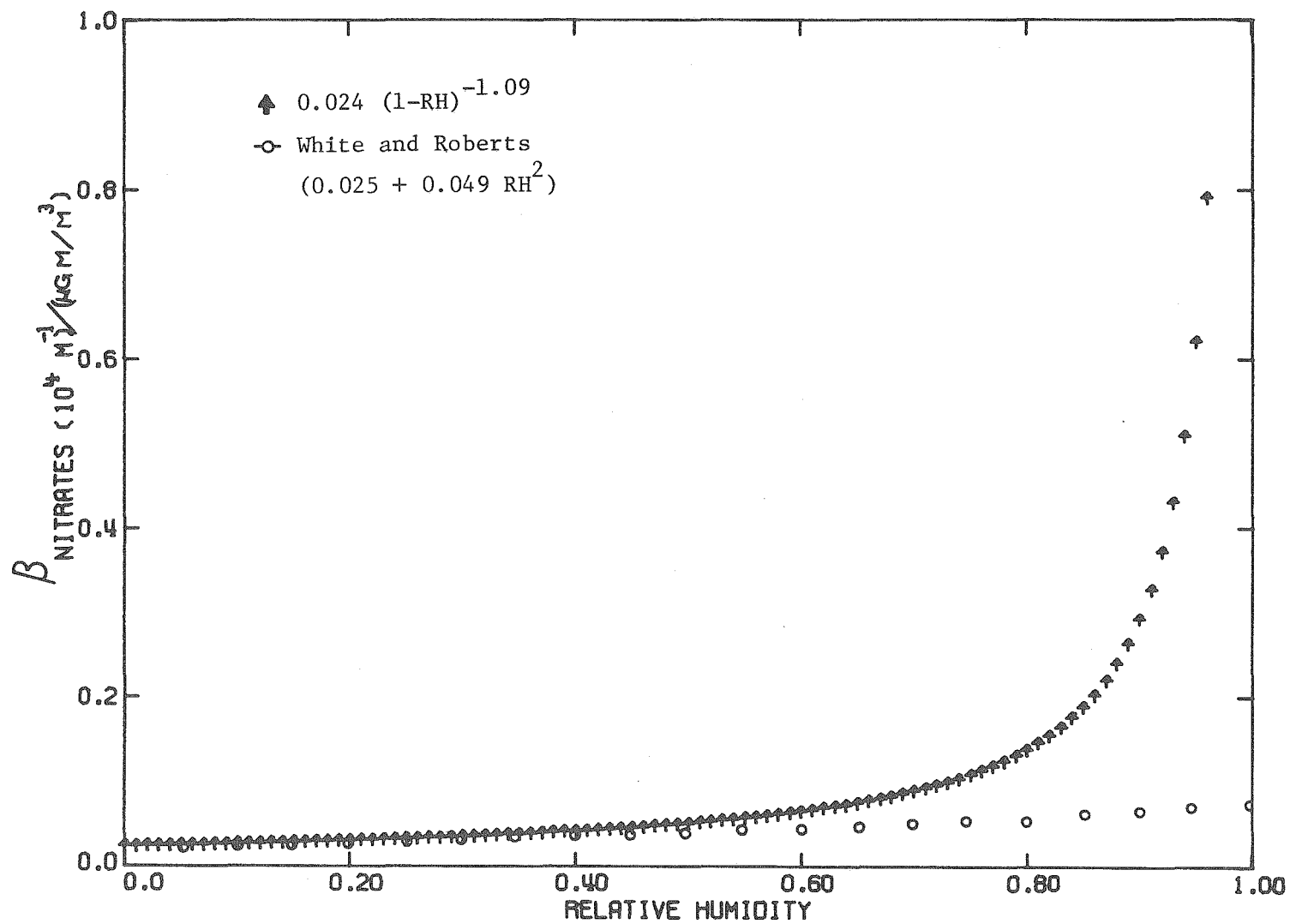


FIGURE 7

of 0.02. Estimation of \bar{b}_j from Koschmieder's formula would then be systematically high by about 25 percent, as would be the values of the coefficients estimated in our regression models. Experimental verification of the relationship between L.A. APCD routine prevailing visibility observations and the atmospheric extinction coefficient, b , would be desirable. That still is unlikely to be a large enough source of error to account for the consistently high coefficient estimates for NO_2 .

The coefficient on NO_2 might well be picking up some of the effects actually due to light scattering by its decay product, NITRATES. This seems quite likely in view of the difficulty in obtaining a significant contribution to light scattering by NITRATES in some of the linear regression models tested, even though most previous investigators have found a strong consistent NITRATE effect. The simple correlation between extinction coefficient and NITRATES is nearly zero, as shown in Appendix II. If light scattering were taken as an independent in situ check on the behavior of the nitrate air monitoring data, then the APCD might be well advised to check their nitrate collection and analysis techniques for possible interferences.

An additional interesting possibility is that NO_2 might be highly correlated with an important aerosol subfraction, perhaps submicron organics, for which explicit data was unavailable for inclusion in the model. The L.A. APCD's historical tape sampler particulate data has been displayed by Phadke, et al. (1975). Their study notes that the diurnal variation of that particulate index is similar to the observed diurnal pattern for carbon monoxide at downtown Los Angeles, and they suggest that the automobile is a major source of particulate matter at that location. If particulate loadings closely follow automotive pollutant levels in general, then the coefficient on NO_2 in our regression models might be expected to be artificially high. If daylight NO_2 values are a better estimator of daylight particulate loadings than

are our 24-hour average (TSP-SULFATES-NITRATES) values, then the difficulty in obtaining a significant estimate of light scattering by non-sulfate non-nitrate particulates in Table III may be explained.

The existence of a persistent daylight peak in Los Angeles particulate concentration would have other implications for this study. If there is a persistent daytime peak in particulate loading of the Los Angeles atmosphere, then the residual difference term $\sum_m \delta_m$ in equation (15), which we neglected, will not have mean zero and random fluctuation about that mean. Rather the 24-hour average particulate measurements will be systematically lower than their 9-hour daytime counterpart corresponding to the period of visibility observations. The result will be that the extinction coefficients per unit concentration estimated from 24-hour averages of the particulate species exhibiting such a daytime peak will be artificially elevated in order to capture this discrepancy. Since aerosol sulfur (and for that matter its precursor, SO_2) is typically seen to exhibit a daytime peak at downtown Los Angeles (Hidy, et al., 1975; Phadke, et al., 1975; Thomas, 1962), the reason for the modest elevation of the estimated sulfate scattering coefficient per unit mass in the models estimated in this paper above those predicted by Garland (1969) and by White and Roberts (1975) may have been identified. In such a circumstance, the qualitative finding of an important sulfate effect on visibility shown by the regressions of Tables II and III would remain valid, while the use of numerical values from Tables II and III for correlation of light scattering with hourly average sulfate concentrations would not be recommended. Our regression equations would remain an unbiased predictor of the likely daylight visibility impact of a strategy aimed at control of 24-hour average particulate levels as long as the relative diurnal variation of pollutant concentrations remained unchanged. Since current State and Federal particulate standards and most historical particulate sampling data are stated in terms of 24-hour and longer concentration averages,

the analysis contained in this study provides useful results in spite of the above potential problems.

Exploring the Visibility Impact of Reduced Sulfate Concentrations

We have seen that our statistical models are probably best behaved with respect to predicting the marginal impact of SULFATES on visibility. The test statistics on the β_{SULFATES} coefficients are consistently significant, confidence intervals on these parameters are narrow, and the shape of the predicted non-linear humidity effect on light scattering by SULFATES is reasonable. The magnitude of the light scattering per unit mass predicted for SULFATES, while perhaps somewhat high, is still understood in relation to theory, the empirical findings of others, and several of the potential sources for error. Whatever problems may exist with estimating the light extinction behavior of other pollutant species, the behavior of light scattering SULFATES is strong enough to stand out clearly from the background noise in the system. This is fortunate, because the motivation behind this study was to explore the impact of altered sulfate concentrations on the long-run distribution of prevailing visibilities at Los Angeles.

With this discussion in mind, the regression model of Table III, entry 4, is used to "backcast" the impact on visibility of decreased sulfates levels at downtown Los Angeles. The sampling period of interest is again our data base of 413 rainless days distributed from August 1965 through December 1974.

Two cases will be considered. In the first instance, the daily average extinction coefficients, b_j , will be synthesized from the regression model using our historic air quality data after having reduced each day's SULFATES value by 50 percent. In the second case, daily SULFATES values will be taken as 25 percent of their actual measured concentrations. This latter case approximates removal of virtually

all of the non-background SULFATES in the Los Angeles atmosphere over the time period considered.³ This is, of course, not to say that one knows how to achieve such a uniform proportionate reduction, but merely to estimate the visibility resulting should such an event have come to pass. An endorsement of any particular control strategy is certainly not implied.

A comparison between the historic cumulative distribution of extinction coefficients and the distributions implied by the SULFATES reduction calculations is presented in Figures 8 and 9. The effect of sulfate reduction in those years is not uniform across the entire distribution of prevailing visibilities. Rather, as is most clearly shown in Figure 9, a 75 percent reduction in SULFATES levels on a daily basis would have reduced the number of days with worse than three-mile visibility by about two thirds, while improvement in the number of days of average visibility greater than ten miles (the California Air Resources Board's visibility target) would be much smaller, about 10 percent.

One likely explanation for this disproportionate SULFATES impact on the days of the very worst visibility is found in Table A of Appendix II. As can be readily seen, suspended sulfate mass loadings are positively correlated with relative humidity. Thus days of high sulfate concentration often coincide with days of high light scattering per unit sulfate mass concentration. Conversely, fairly dry days on which visibility is relatively good were comparatively sulfate free.

In Conclusion

Techniques have been developed for relating air pollution control agency routine air monitoring data to prevailing visibility at downtown

³ Estimation of average $\text{SO}_4^{=}$ background concentrations in the Los Angeles basin is discussed by Trijonis, et al. (1975) and by Hidy, et al. (1975).

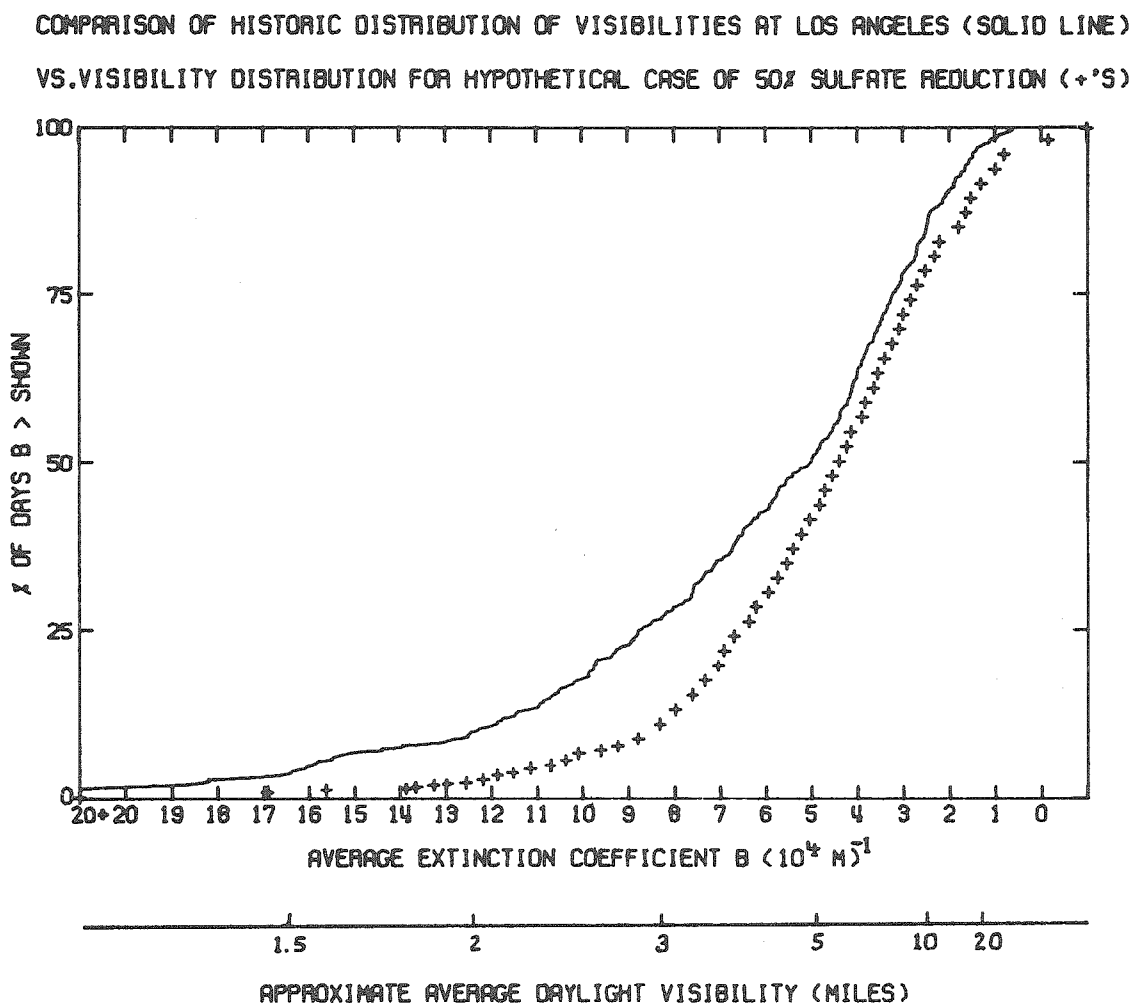


FIGURE 8 Impact of SULFATES reduction, Case I. Cumulative distribution of days on which the average extinction coefficient, \bar{b}_j , exceeded the stated values during the period August 1965 to December 1974 (413 days considered). Solid curve is historic data from L.A. APCD visibility measurements. Broken curve is synthesized from regression model shown in entry 4, Table III after having reduced historic SULFATES levels by 50 percent on each day of observation.

COMPARISON OF HISTORIC DISTRIBUTION OF VISIBILITIES AT LOS ANGELES (SOLID LINE)
VS. VISIBILITY DISTRIBUTION FOR HYPOTHETICAL CASE OF 75% SULFATE REDUCTION (+'S)

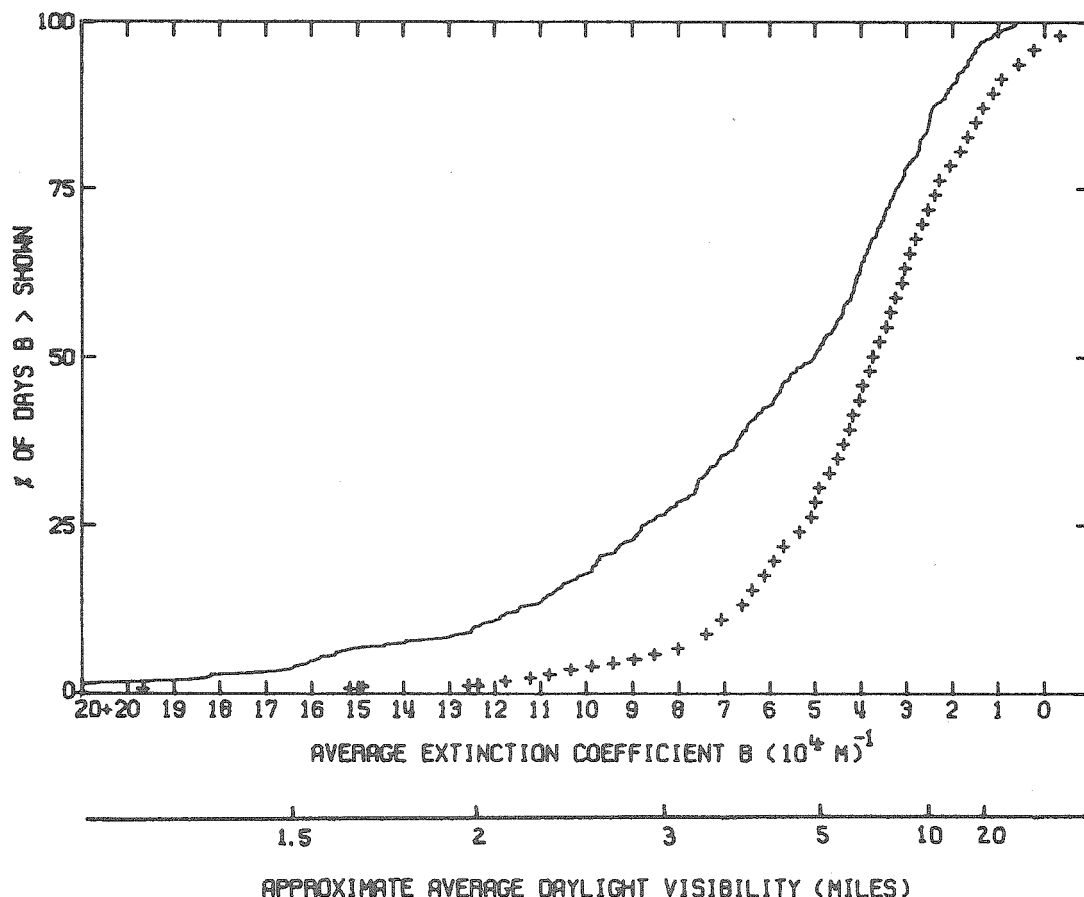


FIGURE 9 Impact of SULFATES reduction, Case II. Cumulative distribution of days on which the average extinction coefficient, \bar{b}_j , exceeded the stated values during the period August 1965 to December 1974 (413 days considered). Solid curve is historic data from L.A. APCD visibility measurements. Broken curve is synthesized from regression model shown in entry 4, Table III after having reduced historic SULFATES levels by 75 percent on each day of observation.

Los Angeles over the decade 1965 through 1974. It was shown that the apparent relationship between light extinction and total suspended particulate mass implied by the long-term historical data base is consistent with the findings of previous short-term special studies. However, total suspended particulate mass was found to be an imprecise estimator of daylight visibility reduction in the Los Angeles area.

When total suspended particulate samples are subdivided chemically, it becomes possible to more closely assess the effect of water-soluble submicron aerosol species, particularly sulfates, on light scattering at Los Angeles. A non-linear regression model for light extinction at Los Angeles was constructed which combines available aerosol chemical information with relative humidity and NO_2 data. Coefficients fitted to that model indicate that there is a pronounced increase in light scattering per unit sulfate solute mass on days of high relative humidity, as would be expected for a hygroscopic or deliquescent substance.

Having developed and fitted a model representing a decade of atmospheric events, it becomes possible to examine the likely long-run response of visibility in the Los Angeles basin to altered levels of particulate sulfates. It is estimated that the visibility impact of reducing sulfates to a half or to a quarter of their measured historic values on each past day of record would be manifested most clearly in a reduction of the number of days per year of worse than three-mile visibility. The number of days of average visibility less than ten miles would be little affected. One reason for the disproportionate impact of the light scattering by sulfates on the days of the worst visibility is thought to result from a high positive correlation between sulfate mass loading and relative humidity. High values of light scattering per unit sulfate mass thus occur on days of high sulfate mass concentration.

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APPENDIX I

Some Previous Investigations of Visibility at Los Angeles

A number of investigators have reviewed visibility observations at Los Angeles with an eye toward determining the causes of reduced visual range. Long-term trends in visibility at Los Angeles are discussed by Neiburger (1955); Kauper, Holmes and Street (1955); Keith (1964); and Keith (1970). These studies conclude that visibility definitely deteriorated at Los Angeles during the period of industrialization which accompanied World War II. Several of these authors observe that this trend toward reduced visibility had been partially reversed by the early 1950's as a result of the initial imposition of pollution controls following the war years. This improvement was apparently not permanent. The most recent study (Keith, 1970) concludes that average noontime visibility at downtown Los Angeles had deteriorated over the past 37 years, and that the trend in this average was still downward as of 1969. Keith (1970) shows that this decline in average visibility is accompanied by a strong increasing trend in the number of days per year with visibilities falling into the ranges 1-1/2 to 2-1/2 miles, and 3 to 6 miles. It is of interest to note that this is the same portion of the cumulative distribution of visibilities which our regression model predicts will be most affected by alterations in atmospheric sulfate levels. (See Figures 8 and 9, this paper.)

Studies of visibility in relation to meteorological parameters have been performed by Renzetti, et al. (1955) and by Neiburger (1955). Documentation of the effects of high relative humidity on light extinction by Los Angeles smog aerosols is provided, and the variations of visibility with wind direction are discussed.

The relation of pollutant concentrations to visibility reduction has been explored. Early research efforts by the Los Angeles Air

Pollution Control District led to the statement that,

"It has been established that a significant percentage of the sulfur dioxide in the atmosphere oxidizes to sulfur trioxide. Preliminary evidence indicates that this acid mist could account for thirty to sixty percent of the total reduction in visibility." (L.A. APCD, 1950)¹

Upon further study, the class of compounds in the aerosol phase potentially responsible for light extinction was found to be quite complex, including a wide variety of hygroscopic liquid droplets, carbon, "tar", opaque particles, plus soluble and insoluble transparent solids (SRI, 1954). The study by Renzetti, et al. (1955) attempted to correlate particulate loading of the atmosphere at Los Angeles and Pasadena with transmissometer measurements of visibility, but with limited success. The statistical section of that report showed that visibility was significantly negatively correlated with a wide variety of pollutant gases and other smog manifestations.

Undoubtedly some of the most interesting investigations are those which sought to relate pollutant emissions to visibility. In 1958, the Los Angeles Air Pollution Control District adopted Rule 62 which resulted in a rapid large scale change from high sulfur fuel use to natural gas combustion by industry in the Basin during the period May through September 1959 (Thomas, 1962). An improvement in visibility due to lowered levels of sulfur-bearing particulates was expected to accompany the SO₂ emission reductions. In a retrospective study of the effects of Rule 62 (L.A. APCD, 1959), little or no improvement in minimum visibility at Los Angeles or Burbank was noted. However, only data at 50 percent or lower relative humidities was considered.² At

¹ It is interesting to compare this statement with the fraction of light scattering at downtown Los Angeles attributed to SULFATES by White, Roberts and Friedlander (1975), as shown in Figure 3 of this paper.

² At least over the decade following 1965 for which a nearly continuous record of sulfate data is available, days of high sulfate are significantly positively correlated with days of high relative humidity. (See Appendix II, this report.) By discarding the data for observations above 50 percent relative humidity, many of the high sulfate days may have been overlooked by the L.A. APCD.

Los Angeles and Long Beach airports, which are closer to major point source locations, significant reduction in the number of days with minimum visibilities of about five miles or less at relative humidity of 60 percent or less was noted. Only about a 4 percent improvement in days of greater than ten-mile minimum visibility occurred at these airport locations. Another study prompted by Rule 62 was performed by Thomas (1962). He correlated visibility at downtown Los Angeles and Burbank, Long Beach and Los Angeles International airports with daily fuel oil consumption on days of poor meteorological dispersion. A small but statistically significant reduction in visibility due to fuel burning was found at Los Angeles International and Long Beach airports. At downtown Los Angeles and Burbank, there was no apparent negative correlation between visibility and fuel oil consumption. Neither of the above studies correlated atmospheric sulfate concentrations with visibility. The lack of visibility improvement at downtown Los Angeles was thus not demonstrated to have accompanied a drop in sulfate levels at that location.

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APPENDIX II

Data Preparation

High volume sampler data on total suspended particulate, sulfate ion and nitrate ion concentrations at downtown Los Angeles was hand copied from the files of the L.A. APCD. The period covered was August 1965 through December 1974. If duplicate samples were available for a 24-hour period, then the arithmetic mean of the two observations was recorded. Following White and Roberts (1975), it was assumed that SULFATES equals 1.3 times $\text{SO}_4^{=}$ concentration and NITRATES equals 1.3 times NO_3^{-} concentration in order to account for the mass of associated cations. Each total suspended particulate (TSP) sample was then subdivided into SULFATES, NITRATES, and (TSP-SULFATES-NITRATES). All units are in micrograms per cubic meter. Data for days on which rain was recorded at downtown Los Angeles were discarded.

Hourly observations on prevailing visibility in miles, relative humidity as a fraction of complete saturation, and NO_2 concentration in ppm were extracted from L.A. APCD data tapes. Data for days on which no corresponding particulate samples existed were discarded. Each remaining day's visibility data were examined, and only those days for which 9 hours of consecutive visibility observations existed were retained. Daily relative humidity and NO_2 data strings were then edited to retain only those hours for which a corresponding visibility observation existed. Since the NO_2 instrument was typically recalibrated around noon-time daily, at least one hour of missing NO_2 data was embedded in each NO_2 data string corresponding to consecutive visibility observations. Missing hourly NO_2 and relative humidity data corresponding to available visibility observations were replaced by the linear interpolation between adjacent valid data points. If more than three embedded consecutive hourly observations were missing, the day's data were discarded.

Missing end points in the NO_2 and relative humidity data strings were replaced by the adjacent value. If the next point adjacent to a missing end point was also missing, the day's data were discarded. The atmospheric extinction coefficient at each hour, b_i , was then estimated from prevailing visibility at that hour by equation (9). Finally the t hour average (nominally $t = 9$) of the extinction coefficient, NO_2 concentration ($\overline{\text{NO}_2}$), and relative humidity ($\overline{\text{RH}}$) was taken for each day of interest. It is important to note at this point that the average extinction coefficient computed in this manner is not equal to the inverse of the average of the day's prevailing visibility observations scaled in proportion to the constant of equation (9). For use in forming the non-linear functions of relative humidity in equation (19), each hourly relative humidity value, RH_i , was retained. At the end of this editing process, 413 days of useful data on all selected variables remained spanning the period August 1965 through December 1974.

A second data base for use with the low humidity model was constructed by a similar procedure. In this case, however, hourly extinction coefficient, NO_2 , and relative humidity observations were edited prior to averaging to remove all data for those hours where relative humidity exceeded 70 percent. If fewer than five hours of low humidity observations remained in a day after this editing procedure, the day's data were discarded. In this second data base, 390 days of observation on all selected variables remained spanning the period August 1965 through December 1974. A statistical description of these data bases follows.

Statistical Description of Data Base Used in this Study

A. Unrestricted Data Base Incorporating all Relative Humidity Values

Number of Complete Sets of Observations = 413 Days

Time Period Spanned is August 1965 through December 1974

	<u>Variable</u>						
	Average** Extinction Coefficient [10 ⁴ m] ⁻¹	SULFATES* μgm/m ³	NITRATES* μgm/m ³	(TSP-SULFATES -NITRATES)* μgm/m ³	NO ₂ ** ppm	Average** Relative Humidity %/100	DUMMY one or zero
Average	6.62	17.54	13.92	127.18	0.100	0.53	0.52
Standard Deviation	5.52	14.80	10.77	50.59	0.050	0.17	0.50

Correlation between Variables

	Extinction Coefficient	SULFATES	NITRATES	(TSP-SULFATES -NITRATES)	NO ₂	RH%/100	DUMMY
Extinction Coefficient	1.00	0.62	0.09	0.25	0.42	0.38	0.11
SULFATES	0.62	1.00	-0.03	0.08	0.22	0.48	-0.17
NITRATES	0.09	-0.03	1.00	0.29	0.42	-0.14	-0.21
(TSP-SULFATES -NITRATES)	0.25	0.08	0.29	1.00	0.48	-0.29	0.14
NO ₂	0.42	0.22	0.42	0.48	1.00	-0.14	-0.15
RH%/100	0.38	0.48	-0.14	-0.29	-0.14	1.00	-0.11
DUMMY	0.11	-0.17	-0.21	0.14	-0.15	-0.11	1.00

*24 hour average.

**t hour average, where t corresponds to the 9 hours of visibility observations available in each day selected.

B. Restricted Data Base Incorporating only those Hours with
Relative Humidity below 70%

Number of Complete Sets of Observations = 390 Days

Time Period Spanned is August 1965 through December 1974

	<u>Variable</u>						
	Average** Extinction Coefficient [10 ⁴ m] ⁻¹	SULFATES* μgm/m ³	NITRATES* μgm/m ³	(TSP-SULFATES -NITRATES)* μgm/m ³	NO ₂ ** ppm	Average** Relative Humidity %/100	DUMMY one or zero
Average	5.65	16.30	14.28	129.47	0.099	0.48	0.51
Standard Deviation	3.83	13.83	10.70	50.37	0.052	0.14	0.50

Correlation between Variables

	Extinction Coefficient	SULFATES	NITRATES	(TSP-SULFATES -NITRATES)	NO ₂	RH%/100	DUMMY
Extinction Coefficient	1.00	0.67	0.11	0.39	0.52	0.31	0.12
SULFATES	0.67	1.00	0.003	0.14	0.24	0.44	-0.13
NITRATES	0.11	0.003	1.00	0.26	0.39	-0.07	-0.25
(TSP-SULFATES -NITRATES)	0.39	0.14	0.26	1.00	0.47	-0.25	0.14
NO ₂	0.52	0.24	0.39	0.47	1.00	-0.13	-0.14
RH%/100	0.31	0.44	-0.07	-0.25	-0.13	1.00	-0.12
DUMMY	0.12	-0.13	-0.25	0.14	-0.14	-0.12	1.00

*24 hour average.

**t hour average, where t = number of hours of visibility observations available that day; nominally t = 9; t_{min} = 5.

APPENDIX III

Summary of Neiburger and Wurtele's Approximation Relating Particle Size to Particle Solute Mass

Light scattering by aerosols is a strong function of particle size. Particle size in turn is heavily influenced by atmospheric humidification if the aerosol material is water soluble.

Relative humidity is defined as the prevailing ambient vapor pressure of water divided by the saturation vapor pressure over a plane pure water surface at the same temperature. Three factors altering the equilibrium vapor pressure over atmospheric droplets from that prevailing over a plane pure water surface are surface curvature, electric charge and dissolved substances. The effect of surface curvature is to raise the equilibrium vapor pressure while the effect of electric charge and dissolved substances is to lower it. If the solution effect dominates, then droplets containing liquid water can persist in the atmosphere at relative humidities below 100 percent.

Neiburger and Wurtele (1949) examined these factors as they affect atmospheric solution droplets of approximately one micron particle diameter. They conclude that the vapor pressure lowering effect of the dissolved substances in such particles will control particle size at humidities below 100 percent. Relying on laboratory data for vapor pressure over solutions of electrolytes, they constructed an expression for the vapor pressure over a solution droplet:

$$(A3.1) \quad \frac{p}{p_o} = 1 - CM$$

where p = the vapor pressure of water over a solution droplet

p_o = the vapor pressure over a plane surface of pure water

M = concentration of solute in the droplet, expressed as gram formula weights of solute per gram of solution.¹

C = a factor which can be computed from experimental data presented in the International Critical Tables. C is not a constant; rather it is a function of concentration, temperature, and the nature of the solute involved.

For the droplet to remain in equilibrium in the atmosphere, the left-hand side of equation (A3.1) is equated to the ambient relative humidity, RH, as follows:

$$(A3.2) \quad RH = 1 - CM$$

The mass concentration of solute in the drop is given by:

$$(A3.3) \quad c = wM$$

where c = mass concentration of solute in the drop expressed as grams of solute per gram of solution

w = solute molecular weight, in grams per gram formula

The mass of solute in one drop is related to its mass concentration, c , by:

$$(A3.4) \quad m_s = \frac{4}{3} \pi r^3 \rho c$$

where m_s = mass of solute in the droplet, grams

r = droplet radius, in centimeters

ρ = droplet density, grams of solution per cubic centimeter

Solving equation (A3.4) for c :

¹The system of units used in Neiburger and Wurtele's paper was not spelled out explicitly. In this recapitulation of their argument, a set of consistent units is supplied. Please note that this unit system differs from that used in the International Critical Tables, and that M as used in (A3.1) is based on solution weight, not solvent weight.

$$(A3.5) \quad c = \frac{3}{4} \frac{m_s}{\pi r^3 \rho}$$

Substituting equations (A3.5) and (A3.3) into equation (A3.2), Neiburger and Wurtele developed an expression for droplet radius:

$$r = K [m_s / (1 - RH)]^{1/3}$$

The factor $K = (3C/4\pi\rho_w)^{1/3}$ was described by Neiburger and Wurtele as "... a parameter of the nuclear substance which has a variation of the order of 1 percent with temperature and concentration." Checking that statement as it applies to solutions of ammonium sulfate and ammonium nitrate, one finds that K is not quite that well behaved. For ammonium nitrate at a reference temperature of 100°C, K decreases by roughly 10 percent as the concentration of solute in the solution is diluted from 24 molal down to about 0.6 molal. The change in K^3 , for example, would be correspondingly more pronounced. Still, the order of magnitude of the change in K seems small compared to the order of magnitude of changes in solute concentration.

The reader should thus be cautioned that the assumption that K is constant is an empirically-based approximation. This approximation is attractive because it yields an uncomplicated hyperbolic expression in relative humidity which is practical for use in a simple non-linear regression model while at the same time preserving some sense of the underlying relationship between particle size and light scattering. For a theoretically-based discussion relating the particle size of solution droplets to ambient relative humidity, see Byers (1965). The reader might also be interested in a recent review article by Hänel (1976) which explores the relationship between theoretical and approximate treatments of particle size as a function of relative humidity.

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APPENDIX IV

Summary of Recommendations for Design of Routine Air Monitoring Programs Aimed at Assessment of the Causes of Visibility Deterioration

Analysis of existing air pollution control agency routine air quality measurements is not only cost-effective; it is usually the only way in which one can say anything about the long-term behavior of an air basin without designing an experiment from scratch and then waiting for the long-term to repeat itself. However, air pollution control agency air monitoring programs usually have not been designed with a visibility study in mind. In attempting to use existing data to reveal the relationship between sulfate air quality and visibility deterioration at a particular air monitoring site, a number of difficulties were encountered and tackled. Comments made in passing on the means for eliminating some of these difficulties are summarized in this appendix.

Particle Size Determination: As shown in Figure 1 of this paper, the light scattering potential of a given mass of atmospheric particulate matter is a strong function of particle size. Particles in sizes between one-tenth microns and two microns in diameter are responsible for the bulk of the light scattering in the Los Angeles atmosphere. In this study, aerosol chemical composition has been used as a key to particle size and solubility. It would be more desirable, however, to obtain data on particle size directly from physical measurements. This can be done by incorporation of inertial impactors into an agency's air monitoring program. Before beginning a size-segregated particulate sampling program, a careful intermethod study would be necessary to select or design an impactor with a sharp cut-off between adjacent stages, and a high enough flow rate to collect a sample volume suitable for chemical analysis.

Chemical Resolution: In this paper, the results of comprehensive chemical analysis of particulate samples taken from the Los Angeles atmosphere as part of previous short-term special studies (e.g., those of Hidy, et al, 1975) served as a pre-survey of the important chemically distinguishable fractions of the local submicron aerosol. Before establishing visibility analysis as one of the goals of its particulate sampling program, an agency should assure itself that data will be collected on all of the abundant submicron chemical species. For example, in the study performed in this paper, the lack of availability of ammonium ion and organic particulate data required that major assumptions be made (based on the findings of others) before the analysis could proceed. When a pre-survey indicates that additional important pollutants require measurement before the visibility study's success can be assured, then the agency should consider allotting resources sufficient to develop laboratory practices and capacity for performing those analyses.

Once the monitoring program is underway, it should be possible to check the chemical measurements against visibility observations to see if any unexpected relationships hint at sampling trouble. In the case of the study pursued in this paper, a near zero correlation between NITRATES and extinction coefficient, plus an exaggerated estimate of the extinction coefficient per ppm for NO_2 , indicate a possible problem with sample collection or analysis which should be investigated further.

Temporal Resolution: A visibility study requires simultaneous information on particulate characteristics, nitrogen dioxide data, relative humidity information, and an estimate of the atmospheric extinction coefficient. Air monitoring and meteorological data bases should be designed so that each necessary measurement can be computed over the same averaging time. Ideally, one would like periodic instantaneous readings on each variable of interest, but that is not feasible with

present particulate sampling technology. Data taken over two-hour averaging times by Hidy, et al. (1975) allowed White and Roberts (1975) to obtain excellent statistical confidence tests in their visibility study. At longer averaging times, information can still be extracted from a statistical study of visibility in relation to aerosol composition, but the unexplained variance in regression model results will possibly increase. Increased sampling frequency is of course more expensive. Perhaps intensive short-term sampling should be confined to a few monitoring stations at which the meteorological measurements needed by a visibility study are also readily available.

Extinction Coefficient Determination: Visual range and extinction coefficient estimates can be made by either instrumental methods or by a human observer. Each of these approaches has its own advantages and disadvantages. However, if one wishes to use these measurements interchangeably, it is important to run a comparative study between the agency's trained observer and instrumentally determined b_{scat} values. As mentioned in the body of this report, less than ideal availability of visibility markers, plus the requirement that markers be clearly recognized and not just seen could lead to a minimum contrast level for reported prevailing visibility observations that deviates from Koschmieder's assumptions.